Synthesis and Characterization of Cobalt(II), Nickel(II) and Copper(II) with [2-(4-Isobutyl-phenyl)-propionic acid N'-{(4-isobutyl-phenyl)propionyl}-hydrazide]

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Abstract

Synthesis of complexes of Cobalt(II), Nickel(II) and Copper(II) with the ligand [(2-(4-Isobutyl-phenyl)-propionic acid N-{(4-isobutyl-phenyl)-propionyl}-hydrazide] (LH) have been prepared and characterized by, atomic absorption spectrophotometer (AAS), Infrared spectra, electronic spectra, molar conductivity measurements and magnetic moment measurements; It has been found that the ligand behaves as a neutral bidentate, Ligand forming chelates with 1:2 (metal: ligand), octahedral structure is suggested in Co(II) and Ni(II) complexes and square planer in Cu(II) complexes according to the analytical results.

Keywords: Diacylhydrazines, Transition metal Complexes, Propionic acid.

1. Introduction

The coordination chemistry of nitrogen-oxygen donor ligands is an interesting area of research[1]. Complexes of substituted hydrazine such as hydrazides, thiosemicarbazides, hydrazones and diacylhydrazines are of general interest as models for bioinorganic processes [2-6]. A search of literature reveals that no more work has been done on complexation of diacylhidrazines. It is well know that these compounds containing two amide moieties which have a strong ability to form metal complexes (Scheme 1). This ligand system shows the keto-enol tautomerism and can acts as mononegative bidentate or mononegative tridentate [7].



In order to study the coordination modes of (LH) with transition metals and its complexes, we

synthesized and characterized some Cu(II), Co(II) and Ni(II) complexes (Scheme 2).



Scheme(2): Route of synthesis of (LH) and the corresponding Cu(II), Co(II) and Ni(II) complexes.

2-Experimental Part

2-1. Physical measurements:

All the chemical substances were supplied by BDH and Fluka are of purity more than 99%. The NMR spectra were registered on a Varian Gemini 300 BB apparatus working at 300 MHz for a 1H and 75 MHz for 13C using TMS as internal standard. Chemical elemental analyses of the ligand was done with Eurovectro EA3000 (for C, H and N). Infrared spectra were recorded by a SHIMADZU infrared spectrophotometer FT-IR model 8400S in the 4000-400 cm⁻¹ Range using KBr disc, ultraviolet spectra were recorded by Shimadzu UV-VIS Recording UV-1800 spectrophotometer using DMF as a solvent, melting points were determined by an electrothermal melting point model 9300, magnetic susceptibilities were measured on instrument type Bruker BM 6 were carried at room temperature by Faraday method, the molar conductivity of the complexes (0.001 M) in DMF were measured using HANNA model 214EC determination conductivity meter, of metals percentage by atomic absorption spectrophotometer on **PYEUNICAM** SP9-atomic absorption spectrophotometer (Phillips).

2-2. Preparation of the ligand:

The [2-(4-isobutyl-phenyl)-propionic acid N-{(4isobutyl-phenyl)-propionyl}-hydrazide] ligand was prepared as following; Added slowly with stirring (0.001mol) of ibuprofen chloride to ibuprofen acid hydrazide in (25 ml) of dry THF. The solution was kept under reflux for 2 hours. Then cooled and poured on crushed ice and neutralized by using 10% sodium bicarbonate, a white solid precipitated directly. The white precipitate was isolated and recrystallized from ethanol .Yield: 76%; m.p.(183-186 °C); Anal. calcd. for $C_{26}H_{36}N_2O_2$ (422.84 g/mol): C, 76.36, H, 8.81, N, 6.85%. Found: C, 76.33, H, 8.85, N, 6.9%; IR (KBr, cm⁻¹): 3218 w (NH), 1604 s (C=O), 3020 w (C-H stretching of aromatic ring), 2956 m (CH₂ as), 883 m (N-N), ¹H-NMR: (DMSOd6) δ at 0.9 (d, (CH₃)₄), 1.8(m, 1H aliphatic), 2.4(d, -CH2-), 1.5(d, 3H aliphatic), 3.6(quartet,1H), 7.1(dd, Ar, J=8.14 for ibuprofen ring), 7.9(s, 2H, NH). ¹³C-NMR: 170 (C=O), 18(CH₃), 22(CH₃)₂, 44(C-H aliphatic), 30(C-H 45(CH2aliphatic), aliphatic tertiary), 127,129(C=C Ar for ibuprofen ring), 136, 141(=C-Ar for ibuprofen ring). 2.3. Synthesis of the complexes:

(1,3,4,6,7 and 9 complexes)

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These complexes were prepared using salts of $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $Co(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$ and $Cu(NO_3)_2.2H_2O$ scheme(2). The ethanolic solution of metal ion salt (1 mmol/5 ml ethanol) was mixed with stirring with a hot clear ethanolic solution of the ligand (**LH**) (2 mmol/20 ml ethanol). After stirring the solution for 3 hrs. The resulting solution, was filtered off and set aside for slow evaporation at room temperature. A precipitates were filtered off and dried in oven.

(2,5 and 8complexes)

These complexes were prepared using CoCl₂.6H₂O, NiCl₂.6H₂O and CuCl₂.2H₂O salts scheme(2). A hot ethanolic solution of metallic ion salt (1 mmol/5 ml

ethanol) was mixed with stirring with a hot clear ethanolic solution of the ligand (**LH**) (2 mmol/20 ml ethanol).. A few drops of triethylamine (Et₃N) was added to the solution with stirring. The mixture was refluxed for 3 hours. The solid precipitates were filtered off, washed with ethanol and distilled water and the precipitates were recrystallized from DMSO.

3.Results and Discussion

The ligand and it's metal complexes were insoluble in water but soluble in organic solvents such as DMSO,DMF, the metal percentage in the complexes and physical data of the ligand and its complexes are given in table (1).

No	Compound	Formula	Color	M.P c ⁰	Yield	%Metal
					%	Calc(found)
	LH	$C_{26}H_{36}N_2O_2$	White	178-180	76	Ι
1-	$[Co(LH)_2Cl_2]$	$C_{52}H_{72}N_4O_4Cl_2Co$	Blue	135-138	54	_
2-	$[Co(L)_2(H_2O)_2]$	C52H74N4O6C0	Brown	128-131	50	7.8 (6.7)
3-	$[Co(LH)_2(NO_3)_2]$	C ₅₂ H ₇₂ N ₆ O ₁₀ Co	Brown	102-105	51	5.7 (5.8)
4-	[Ni(LH) ₂ Cl ₂]	$\mathbf{C}_{52}\mathbf{H}_{72}\mathbf{N}_4\mathbf{O}_4\mathbf{Cl}_2\mathbf{Ni}$	Yellow	248-250 ^d	71	
5-	$[Ni(L)_2(H_2O)_2]$	$C_{52}H_{74}N_4O_6Ni$	Gray	258-261 ^d	66	7.3 (6.7)
6-	[Ni(LH) ₂ (NO ₃) ₂]	$C_{52}H_{72}N_6O_{10}Ni$	yellow	231-234	62	_
7-	$[Cu(LH)_2Cl_2]$	$C_{52}H_{72}N_4O_4Cl_2Cu$	Green	170-173	52	8.1 (6.6)
8-	$[Cu(L)_2(H_2O)_2]$	$C_{52}H_{74}N_4O_6Cu$	Green	163-166	60	8.8 (7.1)
9-	$[Cu(LH)_2(NO_3)_2]$	$C_{52}H_{72}N_6O_{10}Cu$	Green	123-125	50	8.2 (6.2)

Table (1): metal percentage and physical data of ligand and it's complexes.

d= decomposition temperature.

3.1. Infrared spectra:

(1,3,4,6,7 and 9 complexes)

Infrared spectra data of ligand and its complexes are given in table(2). Spectrum of free ligand showed a band at 3218cm⁻¹ for stretching vibration of N-H which was shifted to lower frequencies after complexation 3213-3197 cm⁻¹, indicates that the metal ions coordinate through the nitrogen atom of one of the amide groups . Appearance a new medium intensity bands at 3419 cm⁻¹ - 3443cm⁻¹ in the spectrum of 1,3,4 and 6 complexes due to (OH). This indicates the existence of water in these complexes. The strong band at 1604 cm⁻¹ has been observed due to the uncoordinated free carbonyl amid group [8]. A new strong intensity bands at 1379-1386 cm⁻¹ in the spectrum of 3,6 and 9 complexes which assigned to stretching frequency of $v(NO_3)$ bond [9]. The appearance of bands in the IR region at 419-466 cm⁻¹ in the complexes may be assignable to M-N frequency. Additional bands in the complexes for the region 482-526cm⁻¹ compared with IR spectrum of free ligand have tentatively been assigned to M-O

bond [10,11]. From the obtained results it is clear that the Co(II) and Ni(II) associated with ligand through the nitrogen atom of one amide groups and two molecules of water. While the Cu(II) complexes 7 and 9 associated with ligand through the nitrogen atom of one amide groups only.

(2,5 and 8 complexes)

The bands at 3218 for N-H in free ligand was shifted lower frequencies 3205-3215 cm⁻¹ to after complexation ,and this indicates that the metal ions coordinate through nitrogen atom of one of the amide groups. The strong band at 1604 cm⁻¹ is due to the uncoordinated carbonyl amide groups [12]. The IR spectra of the complexes exhibit a broad bands centered at 3433-3446 cm⁻¹ due to the symmetric and asymmetric stretching modes of coordinated H₂O. Weak bands in the 921–935cm⁻¹ranges represent the modes of coordinated water [13]. The nature of the metal-ligand bonding is confirmed by the newly formed bands in the region 524-534 cm⁻¹ and 414-424 cm⁻¹ in spectra of the complexes, which is tentatively assigned to M-O and M-N vibrations [14].

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	Compounds	U(O-H)	U(N-H)	U(C=O)	U(N-N)	U(C-H) aliphatic	U(C-H) Aromatic	U(NO₃)	H ₂ O Coord	U(M-N)	U(M-O)
	LH	-	3218 m	1604 s	883 w	2956 m	3020 w	-	-	-	-
1-	[Co(LH) ₂ (H ₂ O) ₂ Cl ₂]	3427 m	3197 s	1604 s	883 m	2954 m	3022 w	-	-	459 m	526 m
2-	[Co(L) ₂ (H ₂ O) ₂]	3433 m	3205 m	1606 m	846 m	2954 m	3010 w	-	921 m	421 w	524 m
3-	[Co(LH) ₂ (NO ₃) ₂]	3424 m	3213 m	1602 s	844 m	2954 m	3022 w	1382 s	-	410 w	524 w
4-	[Ni(LH) ₂ (H ₂ O) ₂ Cl ₂]	3443 m	3209 s	1604 s	883 w	2954 m	3024 w	-	-	466 w	526 m
5-	[Ni(L) ₂ (H ₂ O) ₂]	3438 s	3205 m	1593 s	842 w	2958 w	3029 w	-	935 w	424 w	534 w
6-	[Ni(LH) ₂ (NO ₃) ₂]	3419	3193 m	1602 s	883 w	2956 m	3026 w	1379 s	-	416 w	524 m
7-	[Cu(LH) ₂ Cl ₂]	-	3209 s	1604 s	883 w	2956 m	3024 w	-	-	419 w	-
8-	[Cu(L) ₂ (H ₂ O) ₂]	3446 w	3205 s	1604 s	883 w	2956 m	3020 w	-	927 m	414 w	528 m
9-	[Cu(LH)₂(NO₃)₂]	-	3205 m	1602 s	844 w	2958 m	3018 w	1386 s	-	429 w	-

 Table (2): Important infrared spectral bands (cm⁻¹) and their assignments

3-2.Magnetic measurement and electronic spectra. The magnetic moments and spectral data of the prepared complexes are given in table (3). The magnetic moment of Cobalt (II) has been found to be (4.05, 4.44 B.M) which is with the range of octahedral Cobalt (II) complexes [15]. The electronic spectrum of **L** show strong bands in the range (38573-39756)cm⁻¹ which can be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, the electronic spectra of Cobalt (II) complexes show two absorption bands at (13897-16271) cm⁻¹ and (17982-19032) cm⁻¹ these bands were assigned to 4T1g (F) \rightarrow 4A2g (F) (v2) and 4T1g (F) \rightarrow 4T2g (P) (v3) transitions respectively, which are characteristic of octahedral stereochemistry [16,17]. In the Nickel (II) complexes the magnetic

moments (2.95,3.32 B.M) , the spectra of these complexes show transition bands at (15432-16298) cm⁻¹ and (19152-20289) cm⁻¹which suggesting the existence of 3A2g (F) \rightarrow 3T1g (F) (v2) and 3A2g (F) \rightarrow 3T1g (P) (v3) transitions[18, 19], the electronic spectra of complex (**6**)display three absorption bands at 9961, 15783 and 20858 cm⁻¹, which may be assigned to three spin-allowed transitions: ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$ (v1), 3A2g (F) $\rightarrow {}^{3}T_{1g}(P)$ (v2), and ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ (v3) which an octahedral spectral configuration. The magnetic moment value of Copper (II) complexes (1.64,1.72 B.M) which may suggest a square planer structure. Its electronic spectrum show at 15357-16553 cm⁻¹ which may assigned to 2E1g \rightarrow 2T1g transition in square planer structure [15,20].

	Compound	Electronic Spectra cm ⁻¹		ra cm ⁻¹	Transition	μ eff.	Conductivity
		v 1	v 2	v 3		(B.M)	Cm ² .ohm ⁻¹ .mol ⁻¹
	LH	38573	39756		$n \rightarrow \pi^*(v l)$		
					$\pi \rightarrow \pi^*(v 2)$		-
1-	$[Co(LH)_2Cl_2]$		14541	17982	${}^{4}\mathrm{T}_{1g}\left(\mathrm{F}\right) \rightarrow {}^{4}\mathrm{A}_{2g}\left(\mathrm{F}\right)\left(\mathrm{v2}\right)$	4.22	1.7
					${}^{4}\mathrm{T}_{1g}\left(\mathrm{F}\right) \to {}^{4}\mathrm{T}_{2g}\left(\mathrm{P}\right)\left(\mathrm{v3}\right.$		
2-	$[Co(L)_2(H_2O)_2]$		16271	19110	${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)(v2)$	4.44	14.4
					${}^{4}T_{1g}\left(F\right) \rightarrow {}^{4}T_{2g}\left(P\right)\left(v3\right)$		
3-	$[Co(LH)_2(NO_3)_2]$		13897	19032	${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)(v2)$	4.05	2.8
					${}^{4}T_{1g}\left(F\right) \rightarrow {}^{4}T_{2g}\left(P\right)\left(v3\right.$		
4-	$[Ni(LH)_2Cl_2]$		15432	20289	${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)(v2)$	2.95	1.9
					${}^{3}\mathrm{A}_{2\mathrm{g}}\left(\mathrm{F}\right) \rightarrow {}^{3}\mathrm{T}_{1\mathrm{g}}\left(\mathrm{P}\right)\left(\mathrm{v3}\right)$		
5-	$[Ni(L)_2(H_2O)_2]$		16298	19152	${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)(v2)$	3.32	13.8
					${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)(v3)$		
6-	$[Ni(LH)_2(NO_3)_2]$	9961	15783	20858	$^{3}A_{2g}(F) \rightarrow ^{3}T_{2g}(F) (v1)$	3.21	2.7
					${}^{3}A_{2g}(F) \rightarrow {}^{3}T1g(F)(v2)$		
					${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)(v3)$		
7-	$[Cu(LH)_2Cl_2]$		16553		$^{2}\mathrm{E}_{1\mathrm{g}} \rightarrow ^{2}\mathrm{T}_{1\mathrm{g}}$	1.64	1.86
8-	$[Cu(L)_2(H_2O)_2]$		15642		$^{2}\mathrm{E}_{1\mathrm{g}} \rightarrow ^{2}\mathrm{T}_{1\mathrm{g}}$	1.73	13.2
9-	$[Cu(LH)_2(NO_3)_2]$		15357		$^{2}E_{1g} \rightarrow ^{2}T_{1g}$	1.72	2.32

Table (3): magnetic moment, Electronic spectra, Conductivity

3-3. Conductivity measurements:

The molar conductance of the complexes 0.001 M in DMF at room temperature show that all complexes are non-electrolytes [21]. The value in the range 1.7-

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 $16.3 \text{ cm}^2.\text{ohm}^{-1}.\text{mol}^{-1}$ table (3).

According to these results the structural formula of the prepared complexes were proposed as shown in (fig- 1).



Figure (1): the proposed structural formula of the complexes.

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تحضير وتشخيص معقدات الكويلت والنيكل والنحاس الثنائية مع الليكاند[2-(4-ايزوبيوتيل-فنيل)-

برویونیك N - {4 - (-ایزوییوتیل-فنیل)- برویونیل}-هایدرازاید]

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الملخص

يتضمن البحث تحضير معقدات فلزية لايونات الكوبلت (II)، النيكل (II) والنحاس (II) مع اليكاند (2-(4-ايزوبيوتيل-فنيل)-بروبونيك 4[- N -(-ايزوبيوتيل-فنيل)- بروبونيل]-هايدرازايد) شُخص الليكاند المحضر بواسطة التحليل الدقيق للعناصر ومطيافية الاشعة تحت الحمراء ومطيافية الرنين النووي المغناطيسي لـC, 131H (ما المعقدات المحضرة فقد تم تشخيصها بواسطة مطيافية الاشعة متحت الحمراء ومطيافية فوق البنفسجية والحساسية المغناطيسية والتوصيلية الكهربائية والامتصاص الذي.

حيث حضر جزء من هذه المعقدات في وسط متعادل بينما الجزء الاخر في وسط قاعدي وبنسبة 2:1 واثبتت النتائج ان هذا الليكاند يرتبط بالايون الفلزي بشكل أحادي السن حيث يرتبط هذا الليكاند بالفلز عن طريق احدى ذرتي النيتروجين. كما بينت النتائج ان جميع معقدات الكوبلت والنيكل كانت ذات شكل ثمانيي السطوح بينما كانت اشكال معقدات النحاس ذات شكل مربع مستوي.